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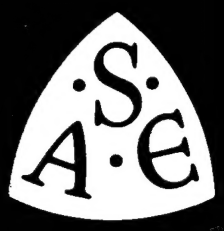

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Factors Affecting High and Low Temperature Performance in Liquid Reaction Molded Urethane Elastomer

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Introduction

Liquid Reaction Molding (LRM) is the terminology presently being used to describe the in situ molding of a finished part from reactive liquid components. This process is particularly suited to the utilization of urethane technology because of the availability of a variety of liquid polyol and isocyanate intermediates, and the high degree of reactivity of these intermediates. Urethane systems also offer a degree of formulation latitude and physical property performance not attainable by other types of polymers.

A major process currently being used to prepare large, molded polymeric parts is injection molding. This process utilizes pre-made polymers designed to perform in the designated end-use application. For most applications, the high molecular weight of these polymers requires high processing temperatures to reduce the polymer to a molten state with a viscosity suitable for the injection process. Even under these conditions, the high viscosity of most polymer melts requires the use of high torque extruders and very high tonnage mold clamps to successfully mold large parts. Utilization of this process requires a large investment in both tools and clamps in addition to the molding machinery.

In contrast to this, consider the preparation of large, intricate parts using urethane LRM technology. Since the individual components are low viscosity liquids, excellent mold fill-out is obtained without high temperatures or pressures. In general, operating pressures are very low ($\sim$ 50 psi in the mold) and temperatures can vary from ambient to 150°F depending on the reactivity and viscosity of the system. Liquid Reaction Molding does require specially designed machinery to deliver and blend the liquid components accurately at high through-put rates. Such machinery is available today from manufacturers such as Hennecke, Krauss-Maffei, Cannon, VTE, and USM. Tooling to be used in preparing LRM parts is significantly lower in cost than tools for injection molding because lower clamp pressures are required during a molding cycle.

The greatest potential for urethane LRM lies in those areas demanding high-speed fabrication of relatively large, intricate, high-performance parts. One area of primary interest is in the automotive industry where sight shields, fender extensions, filler panels and many other similar parts could easily be made using LRM technology. Although these items are important, perhaps the most interesting potential for LRM lies in the production of large parts such as automotive fascia, door panels and fenders. The fascia is basically a cosmetic shell which is not designed to absorb any significant amount of energy but rather to deflect on impact and return to its original position undamaged. Table I shows some of the proposed requirements for a fascia polymer.

Given that the polymer can be prepared using the LRM approach, and that it has all of the requisite ambient temperature physical properties, the polymer must also function over a temperature range from -20°F to $\sim$ 120°F. This requirement is even more rigorous in that it is specified that the polymer shall not crack when impacted at 5 mph at -20°F. This, of course, requires that a polymer be designed with the lowest

ABSTRACT

High and low temperature performance of various urethane elastomers is discussed in terms of compatible/incompatible polymer theory.

The influence of polyol molecular weight, low molecular chain extender and isocyanate are presented and discussed in terms of their effect on the modulus/temperature sensitivity of the elastomers studied.

possible glass transition temperature and the highest modulus consistent with performance requirements. In essence, the modulus must be high enough to make the polymer useful, and it should be as insensitive as possible to changes in temperature.

A discussion of the parameters affecting the performance of polymer modulus as a function of temperature must center around the glass transition temperature(s) (Tg) of the system. Factors controlling Tg will generally have a profound effect on the properties of a given polymer at any specified test temperature, i.e., factors raising Tg above the test temperature will raise the polymer modulus, while factors lowering Tg below the test temperature will lower the modulus.

When considering homopolymer blends (A + B) or copolymers $(AB)_n$, the factor controlling the Tg of the composite is the relative compatibility of A and B. The possibilities for a typical A/B system are shown in Figure 1. Curve 1 is what would be expected if A and B were completely incompatible. Curve 2 shows what would be expected if the components A and B were completely compatible. In this case, the Tg of the composite shifts dramatically depending on the Tg and concentration of the individual components. Curve 3 is the type of behavior usually seen when studying many A/B type systems. It implies that the compatible/incompatible trends in the system were not well defined, and that the modulus of the polymer is changing as a function of temperature. Such trends are indicative of potential problems if the polymer must be functional (i.e., its modulus must be within certain limits) over the temperature range studied.

In a general sense, polyurethane elastomers may be considered block copolymers of the $(AB)_n$ type. The A component is usually a relatively high molecular weight flexible polyether or polyester, while the B component, or "hard segment", contains a high concentration of urethane groups generated from the reaction of a low molecular weight chain extender (usually a glycol) and an isocyanate.

The most obvious application for this multi-component type analysis in urethane systems is in the area of the thermoplastic urethane elastomers. These linear polymers have been studied extensively, and the results reported previously(1).* The LRM polymers of interest in this discussion differ from their thermoplastic counterparts in several important ways: The soft segment in an LRM polymer is a polyoxypropylene glycol, the isocyanate is usually a quasi prepolymer (based on either TDI or MDI) and the elastomer itself is crosslinked due to functionality in one or more of the components. Although these differences are significant, the compatible/incompatible nature of the hard and soft segments still plays an important role in their overall performance.

Experimental

The polymers in this study were prepared using a hand casting technique. The polymer/polyol [2], low molecular weight extender glycol and catalyst (0.01 to 0.03 pt dibutyltin dilaurate) were added to a 500 ml four-necked round bottom flask

*Numbers in parenthesis designate references at end of paper.

equipped with a mechanical stirrer, thermometer, heating mantle and vacuum inlet. The polyol blend was heated to 120°F and evacuated for 30 minutes to assure complete degassing. The stirrer was then shut off, the vacuum broken and the requisite amount of isocyanate added. Vacuum was reapplied and the stirrer started. The system was mixed for ~30 seconds and the liquid poured between glass plates (previously treated with mold release) separated by a 125 mil Teflon spacer. The mold was then clamped and the polymer force cured in the oven for 16 hours at 212°F. Physical properties were determined on an Instron Tensile Tester using ASTM standard methods.

Discussion

LRM Components

Polymer/polyols were chosen as the polyol component in the elastomers prepared for this study. These low viscosity polyols are based on ethylene oxide capped poloxypropylene glycols, and contain 20 weight percent in situ polymerized vinyl polymer(2). They were chosen because of the additional modulus imparted to the elastomer due to the presense of the vinyl polymer. The polymer/polyols have the same composition with the exception that the nominal molecular weights vary over the range from 3750 to 6000 to 7650. This allows an analysis of the effect of polyol molecular weight on polymer preoperties.

Three chain extenders were employed. They include; the 2 mole adduct of ethylene oxide on aniline (NIAX Polyol HL-565), 1,4-butanediol (BDO) and ethylene glycol (EG). They were chosen to allow a determination of the effect of extender molecular weight (EG and BDO) and a large pendant group (HL-565) on the polymer.

Isocyanates studied include a TDI quasi prepolymer with a functionality >2 (30.7% free NCO) and two MDI based quasi prepolymers both with free NCO contents of 23%. Comparison of the properties of polymers containing these isocyanates allows an analysis of the effects of TDI versus MDI.

The formulations and physical properties of the elastomers prepared are shown in Tables II and III. To obtain the most meaningful results in terms of a practical evaluation, an attempt was made to formulate the polymers to approximately the same Shore D hardness. As the data indicate, the elastomers average ~60 Shore D which allows a fair comparison for all of the polymers in this hardness range.

Flexural modulus values over the temperature range of -20°F, 0°F, 72°F and 150°F are also given. This property was chosen because it gives an indication of how the modulus of the polymer changes as a function of temperature. Of course, based on the previous discussion, ideally the polymers would exhibit the behavior illustrated in curve ① of Figure 1. In the elastomers of this study, the "soft segment" is considered the polyether polyol. These polyols normally show a Tg at ~ -40 to -45°F. The "hard segment" is the result of combining the low molecular weight extender and the isocyanate, and usually show Tg's ranging from ~ 130 to >250°F. Thus, a curve similar to curve ① for any of the polymers in Tables II and III would show a loss in

modulus at -45 to -40°F, a flat response of modulus to temperature up to the Tg of the hard segment, and then an additional loss of modulus. Obviously, for optimum performance over a temperature range, this type of behavior is preferred.

Plots of flexural modulus as a function of temperature for several polymers are shown in Figure 2, 3 and 4. These polymers are based on a single isocyanate (the TDI quasi prepolymer), and contain each of the extenders and polyols discussed previously. Taken collectively, these data suggest that both polyol molecular weight and type of extender play an important role in the modulus/temperature performance of these polymers. These effects are clearly seen over the entire temperature range from -20°F to +150°F. Increasing polyol molecular weight (Figures 2, 3 and 4) has the doubly benificial effect of lowering the modulus at -20°F, while increasing the modulus at 150°F. Such results strongly suggest that increasing polyol molecular is decreasing the compatability of the hard and soft segments, resulting in a more fully defined $(AB)_n$ system where A and B are incompatible.

Comparing the slopes of the modulus temperature curves in Figures 2, 3 and 4 also shows the relative effects due to the three different extenders; HL-565, BDO and EG. Modulus variation in those polymers containing HL-565 is greatest, followed by those containing BDO and then those based on EG. The differences observed between polymers containing BDO and EG are real, but not as large as those observed with HL-565. The data indicate that HL-565 containing hard segment is significantly more compatable in the polyether polyol than hard segments based on either BDO or EG. This is most probably due to a plasticizer-like effect exerted by the bulky, pendant benzene ring in this extender. The more subtle differences observed between BDO and EG are most likely due to the higher polarity per unit volume in the EG containing polymer. Such higher polarity should result in higher hard segment/hard segment interactions and hence lower compatibility.

The data from Figures 2, 3 and 4 are plotted somewhat differently in Figures 5 and 6. The effect of the formulation variables just discussed is shown by plotting flexural modulus at a specified temperature (-20 and +150°F) as a function of polyol molecular weight for polymers containing the different extenders. The effects discussed previously are evident.

The effect of isocyanate type on the modulus/temperature performance of various urethane elastomers has also been studied. In this series of polymers, the polymer/polyol was fixed (7650 MW) and both the extender and isocyanate were varied. Modulus/temperature curves for these elastomers are shown in Figures 7 through 9. Comparison of these curves shows that going from HL-565 to BDO to EG, results in a trend very similar to that observed previously. Independent of the isocyanate, HL-565 containing polymers show a higher degree of temperature sensitivity than do polymers containing BDO. These, in turn, are more sensitive to temperature than those containing EG. The direct comparison of the isocyanates in each figure gave some rather surprising results. Generally, the MDI based polymers showed essentially the same modulus/temperature profile when comparing a given extender. Interestingly, in two of the three comparisons (Figures 7 and 9), the TDI containing polymer was found to

have a modulus somewhat less sensitive to temperature variation than those containing MDI. Initially, it was felt that the higher symmetry of the MDI systems would allow better intermolecular alignment, higher modulus and perhaps a flatter modulus/temperature profile. This does not appear to be the case. In fact, the modulus/temperature behavior is essentially no different than similar polymers containing TDI, and, equally surprising, the MDI polymers require significantly more hard segment to attain a given hardness (Tables II and III). The explanation for this behavior is not known.

Summary: Polyol molecular weight and the nature of the low molecular weight chain extender play an important role in affecting the modulus/temperature. Polymers whose modulus is relatively invariant with temperature can be prepared using high molecular weight polyols in conjunction with very low equivalent weight extenders. Interestingly, polymers based on TDI show overall performance characteristics at least similar and in some cases superior to those based on MDI. Overall comparison of the systems studied can be discussed in terms of the relative compatibilities of the hard and soft segments of the formulated polymers.

References

(1) a. F. E. Critchfield, J. V. Koleske and R. A. Dunleavy, "Thermoplastic Urethane Elastomers", Rubber World, August, 1971.

b. F. E. Critchfield, J. V. Koleske, G. Magnus and J. L. Dodd, "Effect of Short Chain Diol on Properties of Polycaprolactone Based Polyurethanes", J. Elastoplastics, Vol. 4, January, 1972.

c. F. E. Critchfield, J. V. Koleske and C. G. Seefried, Jr., "Thermoplastic Polyurethane Elastomers - Temperature Dependence of Physical Properties", Paper No. 730602 presented at the Automobile Engineering Meeting, Society of Automotive Engineers, Detroit, Michigan, May 14-18, 1973.

(2) The polymer/polyols in this study are ethylene oxide capped polyoxypropylene glycols each containing 20 weight percent of in situ polymerized vinyl polymer. Respective hydroxyl numbers and nominal molecular weights are as follows: OH No. 45, NW = 3750; OH No. 28, NW = 6000; OH No. 22, MW = 7650.

TABLE I

REQUIREMENTS FOR FASCIA CANDIDATES

1. Must be flexible, easily paintable and mar resistant.

2. Must be self supporting from -20 to +140°F.

3. Must have the following physical properties.

   a. >150% elongation

   b. Shore D hardness 45

   c. Flex modulus

-20°F	150,000 psi max.
72°F	15,000 psi min.
150°F	>5,000 psi min.

   d. Pass -20°F impact (5 mph)

Figure 1

Modulus vs temperature considerations in various polymer systems -- $\left[(AB)_n\right]$ type

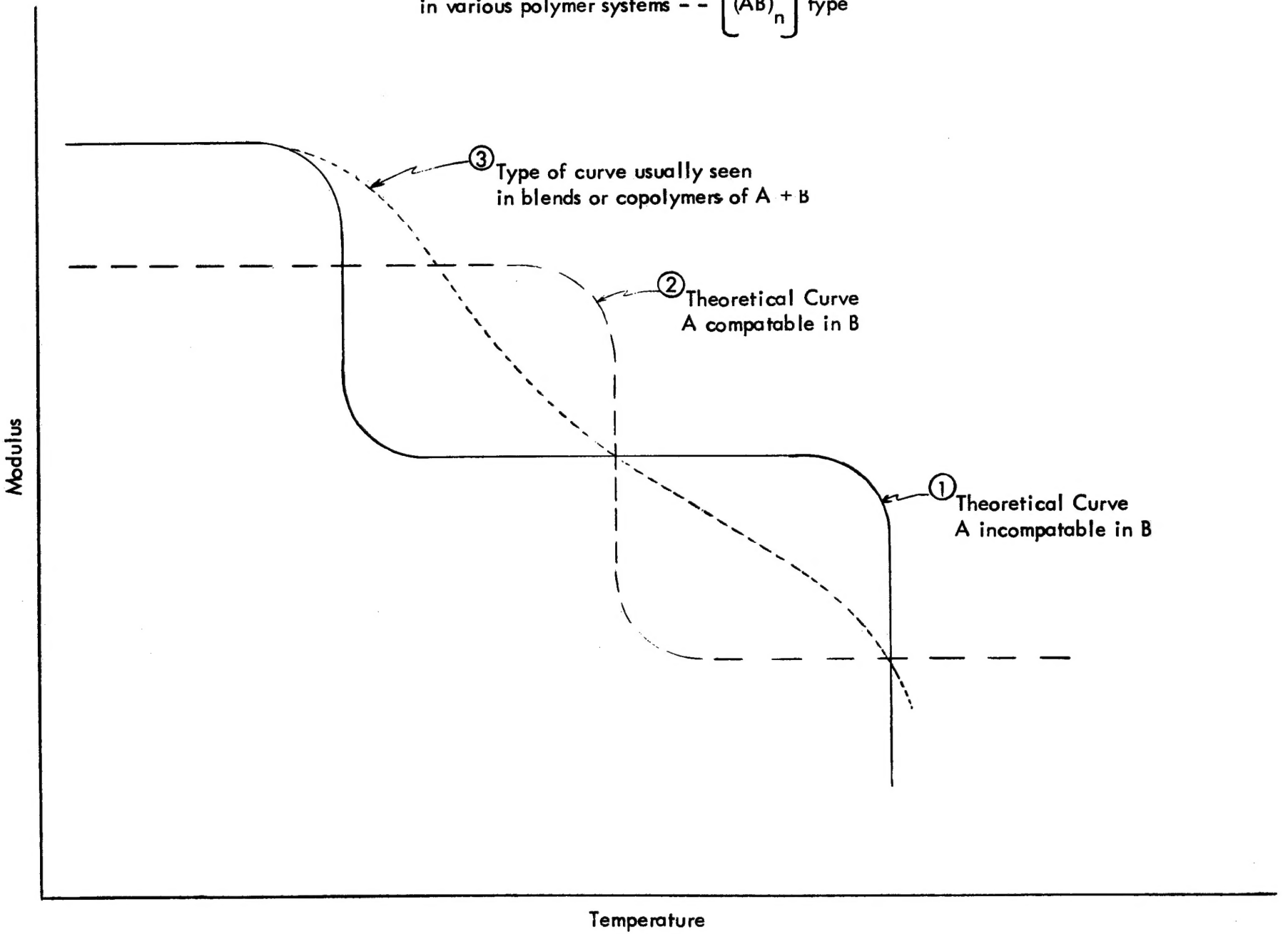


Figure 2

Effect of HL-565 and polymer/polyol molecular weight on the modulus/temperature performance of a urethane elastomer

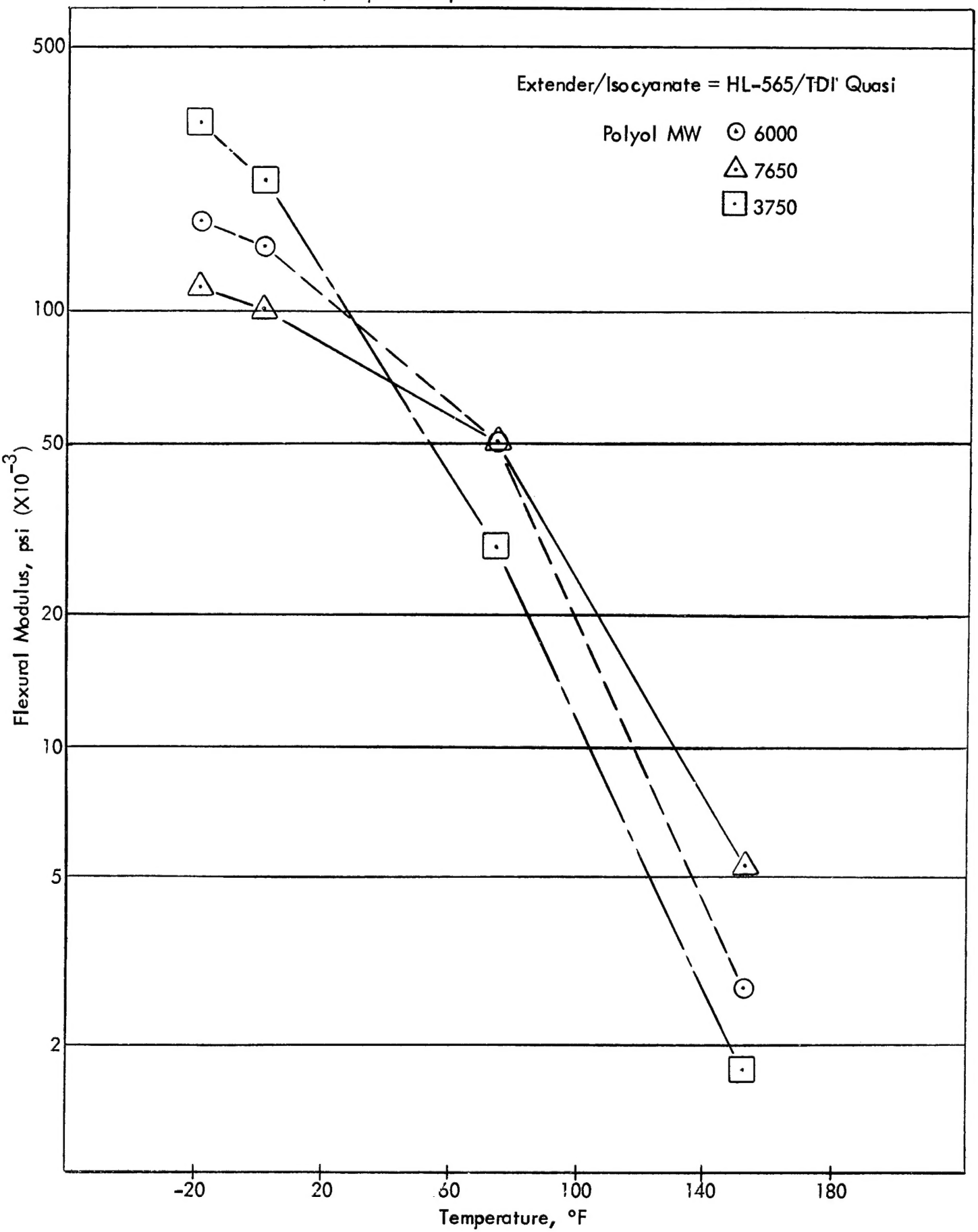


TABLE II

Polymer/Polyol (MW)[a]									
3750	75	-	-	85	-	-	90	-	-
6000	-	75	-	-	85	-	-	90	-
7650	-	-	75	-	-	85	-	-	90
Extender									
HL-565[b]	25	25	25	-	-	-	-	-	-
1,4-Butane diol	-	-	-	15	15	15	-	-	-
Ethylene glycol	-	-	-	-	-	-	10	10	10
Isocyanate									
TDI Quasi,[c]									
Functionality >2	105 I	105 I	105 I	105 I	105 I	105 I	105 I	105 I	105 I
Weight % Hard Segment[d]	48	47	46.5	45	44.6	44	44	41	40.4
Properties									
Shore D Hardness[e]	63	64	61	59	60	60	61	62	61
Flexural Modulus, psi[f]									
-20°F	276M	162M	115M	173M	109M	96M	191M	107M	90M
0	202M	142M	103M	120M	83M	85M	133M	85M	82M
72	29M	52M	51M	21M	38M	49M	33M	46M	55M
150	1.7M	2.7M	5.4M	2.5M	8.1M	17M	4.3M	12M	21M

(a) Nominal Molecular Weight

(b) 2 mole adduct of ethylene oxide on aniline

(c) Free NCO = 30.7%

(d) Weight percent, extender plus isocyanate

(e) ASTM D-2240

(f) ASTM D-790

TABLE III

Polymer/Polyol (MW)									
7650	75	75	75	85	85	85	90	90	90
Extender									
HL-565	25	25	25	-	-	-	-	-	-
1,4-Butanediol	-	-	-	15	15	15	-	-	-
Ethylene Glycol	-	-	-	-	-	-	10	10	10
Isocyanate									
TDI Quasi	105 I	-	-	105 I	-	-	105 I	-	-
M-323	-	105 I	-	-	105 I	-	-	105 I	-
I-180	-	-	105 I	-	-	105 I	-	-	105 I
Weight % Hard Segment	47	51	51	44	50	50	40.4	46.5	46.5
Properties									
Shore D Hardness	61	64	64	60	59	61	61	58	57
Flexural Modulus, psi									
-20°F	115M	181M	200M	96M	121M	126M	90M	80M	77M
0	103M	156M	169M	85M	101M	112M	82M	62M	60M
72	51M	50M	51M	49M	46M	61M	55M	35M	35M
150	5.4M	1.2M	2.0M	17M	12M	29M	21M	15M	18M

Figure 3

Effect of BDO and polymer/polyol molecular weight on the modulus/temperature performance of a urethane elastomer

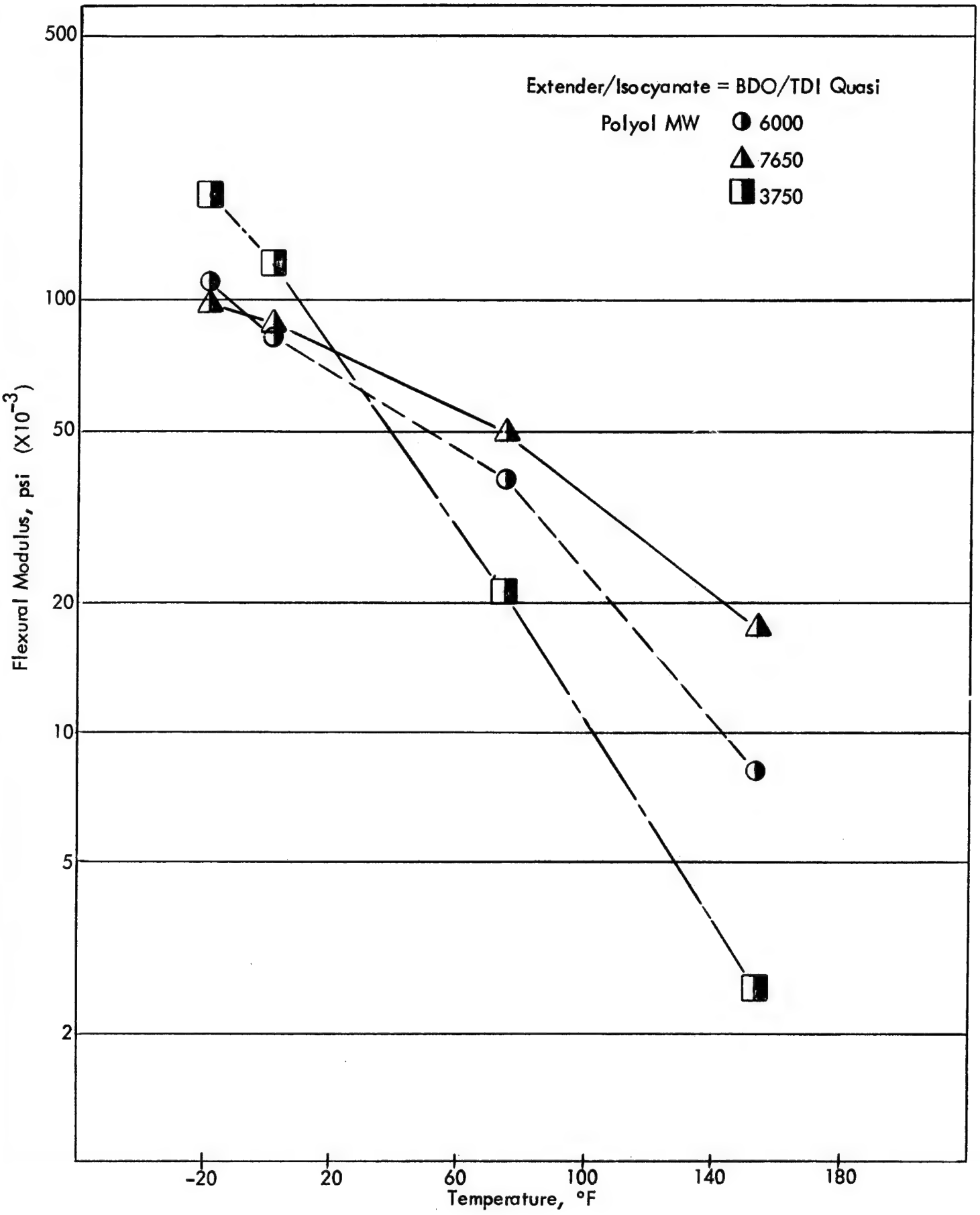


Figure 4

Effect of EG and polymer/polyol molecular weight on the modulus/temperature performance of a urethane elastomer

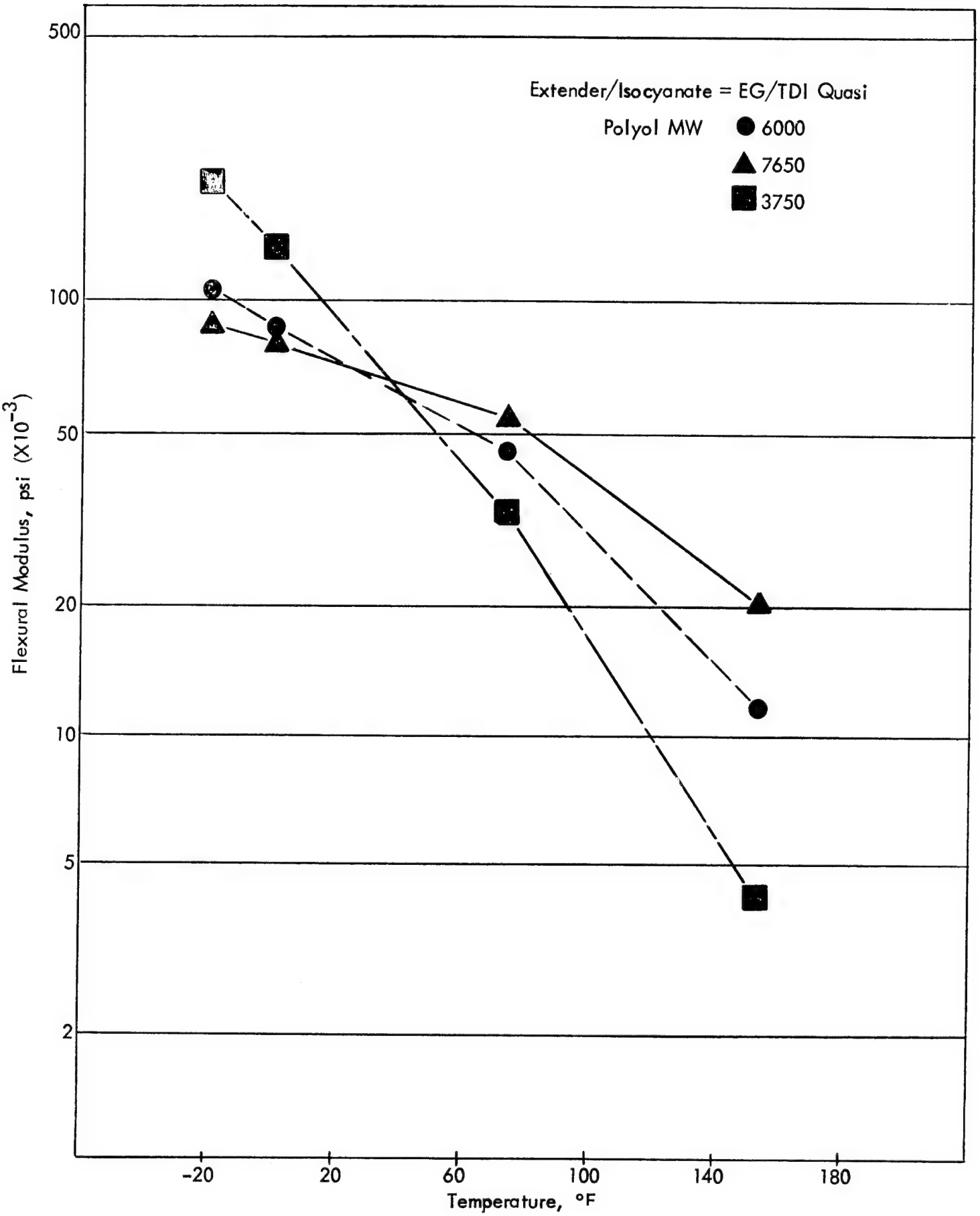


Figure 5

150°F Flexural modulus as a function
of polymer/polyol molecular weight and extender

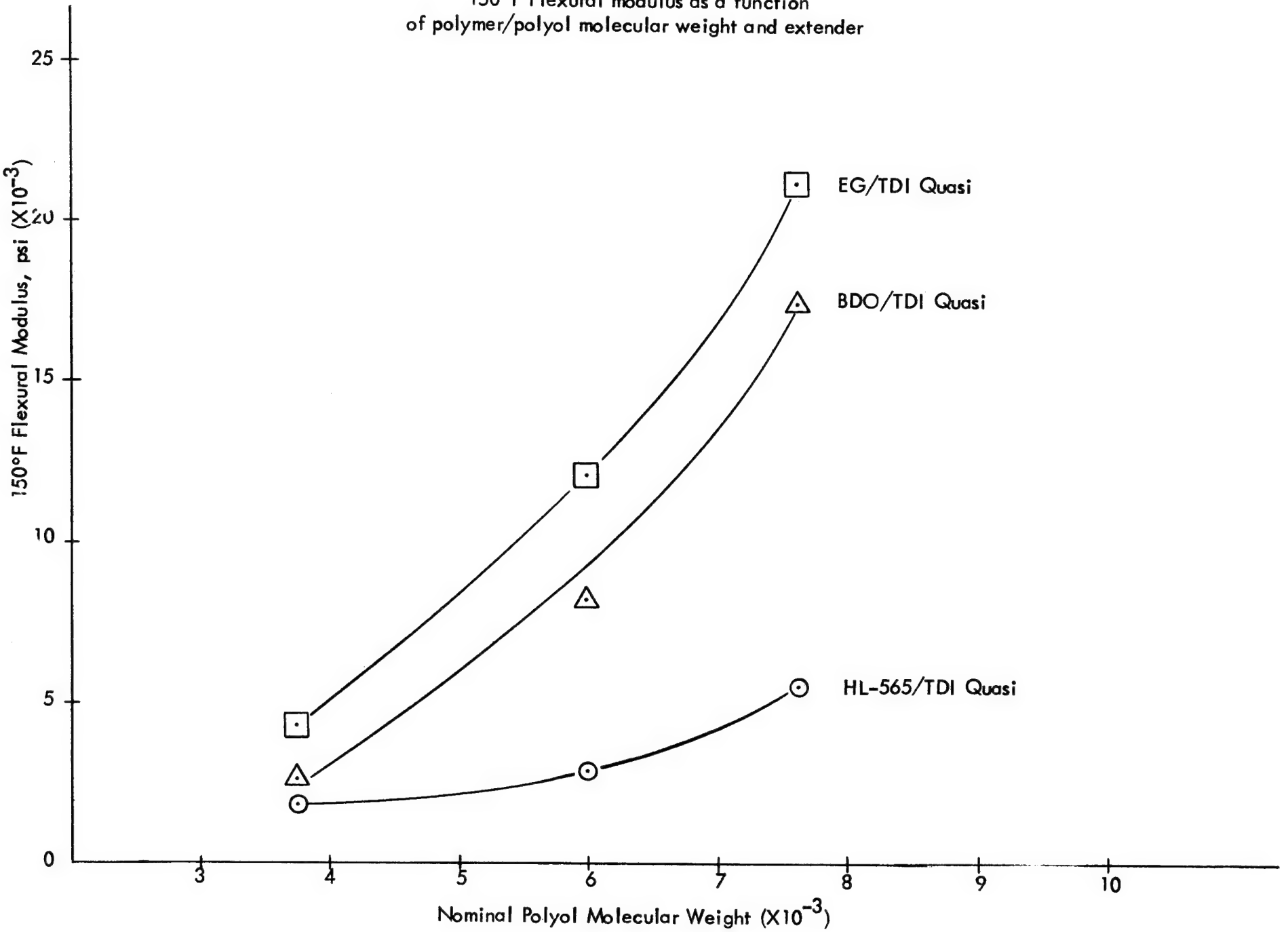


Figure 6
-20°F Flexural modulus as a function
of polymer/polyol molecular weight and extender

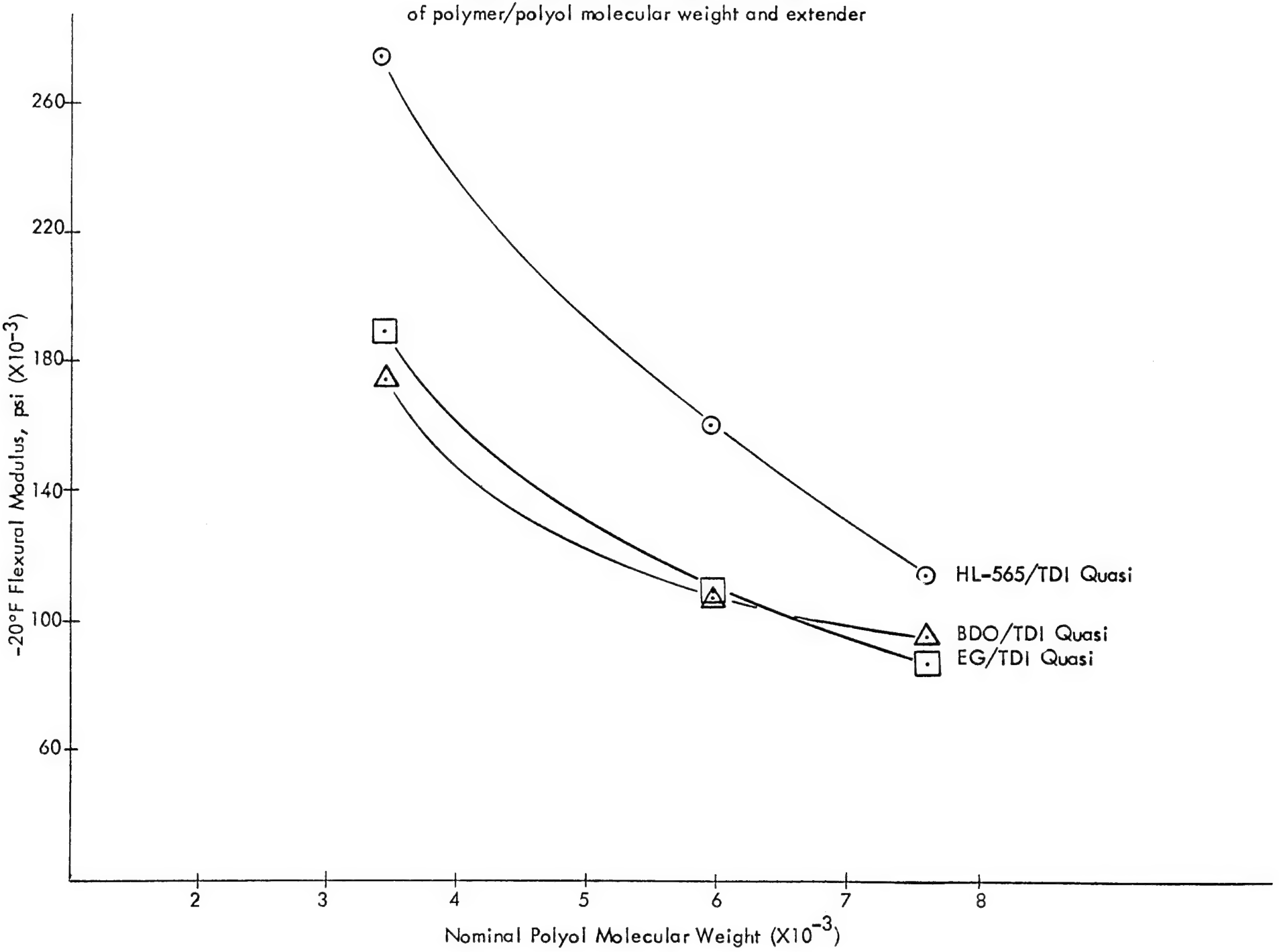


Figure 7

Effect of HL-565 and isocyanate type on the modulus/temperature performance of a urethane elastomer

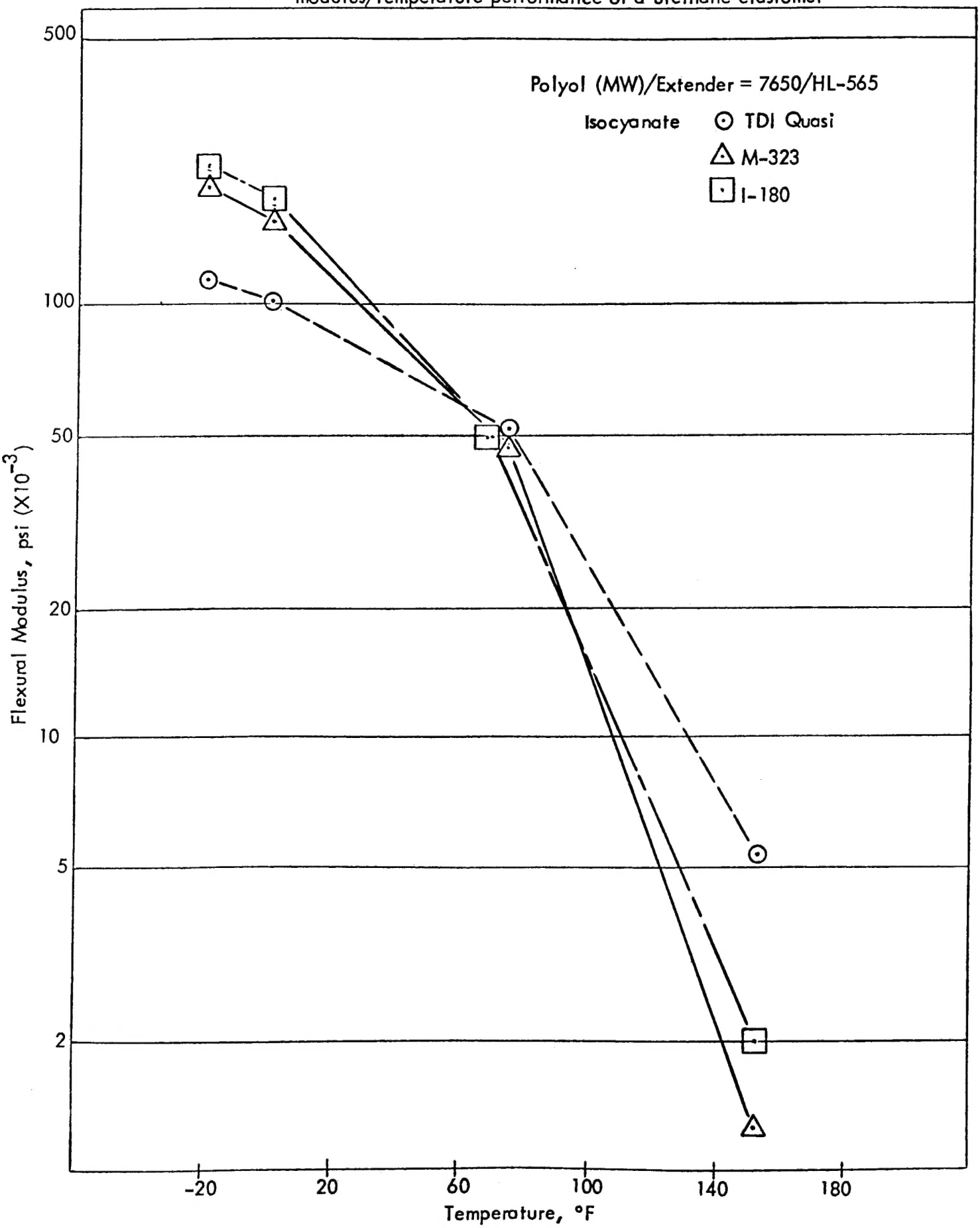


Figure 8

Effect of BDO and isocyanate type on the
modulus/temperature performance of a urethane elastomer

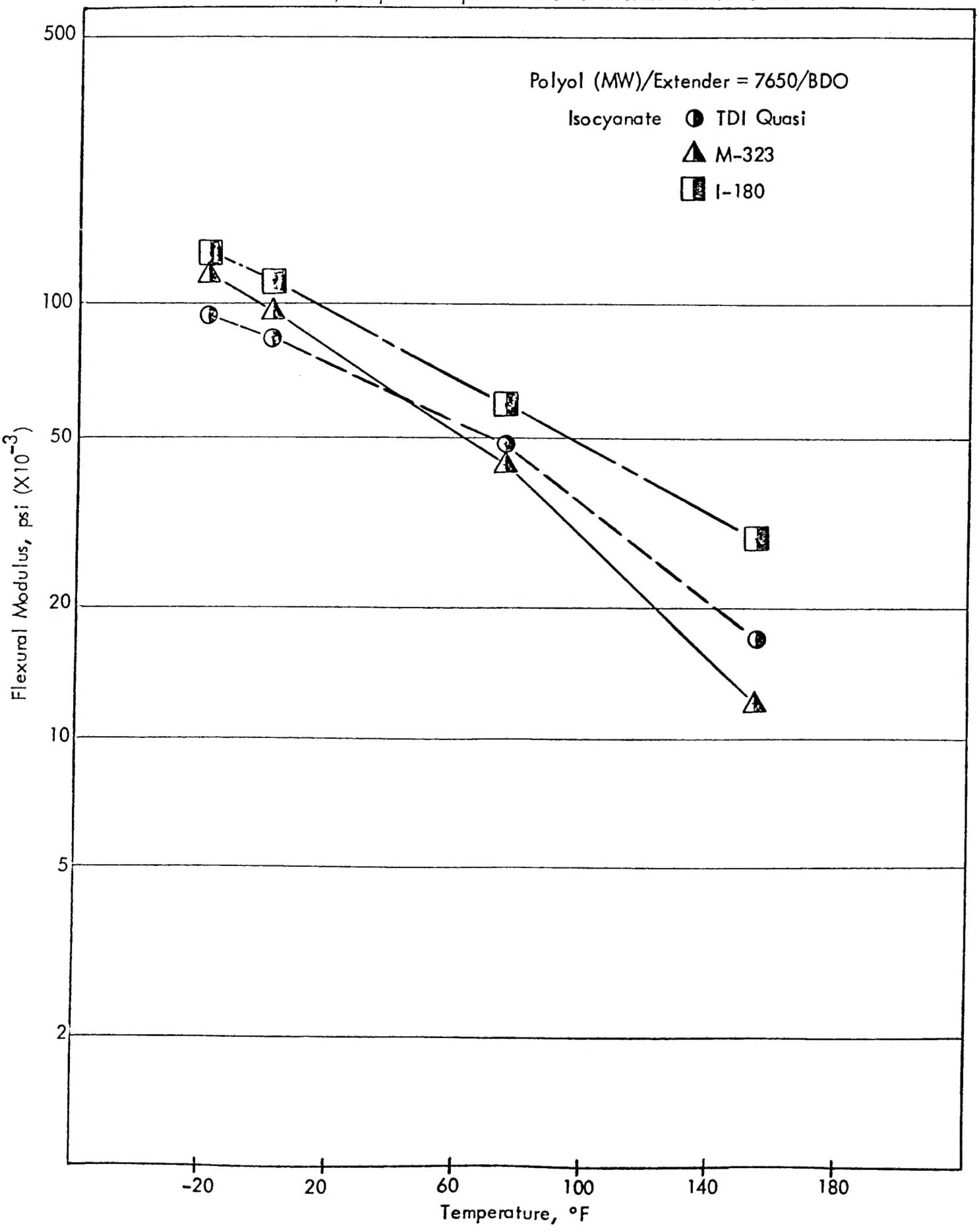
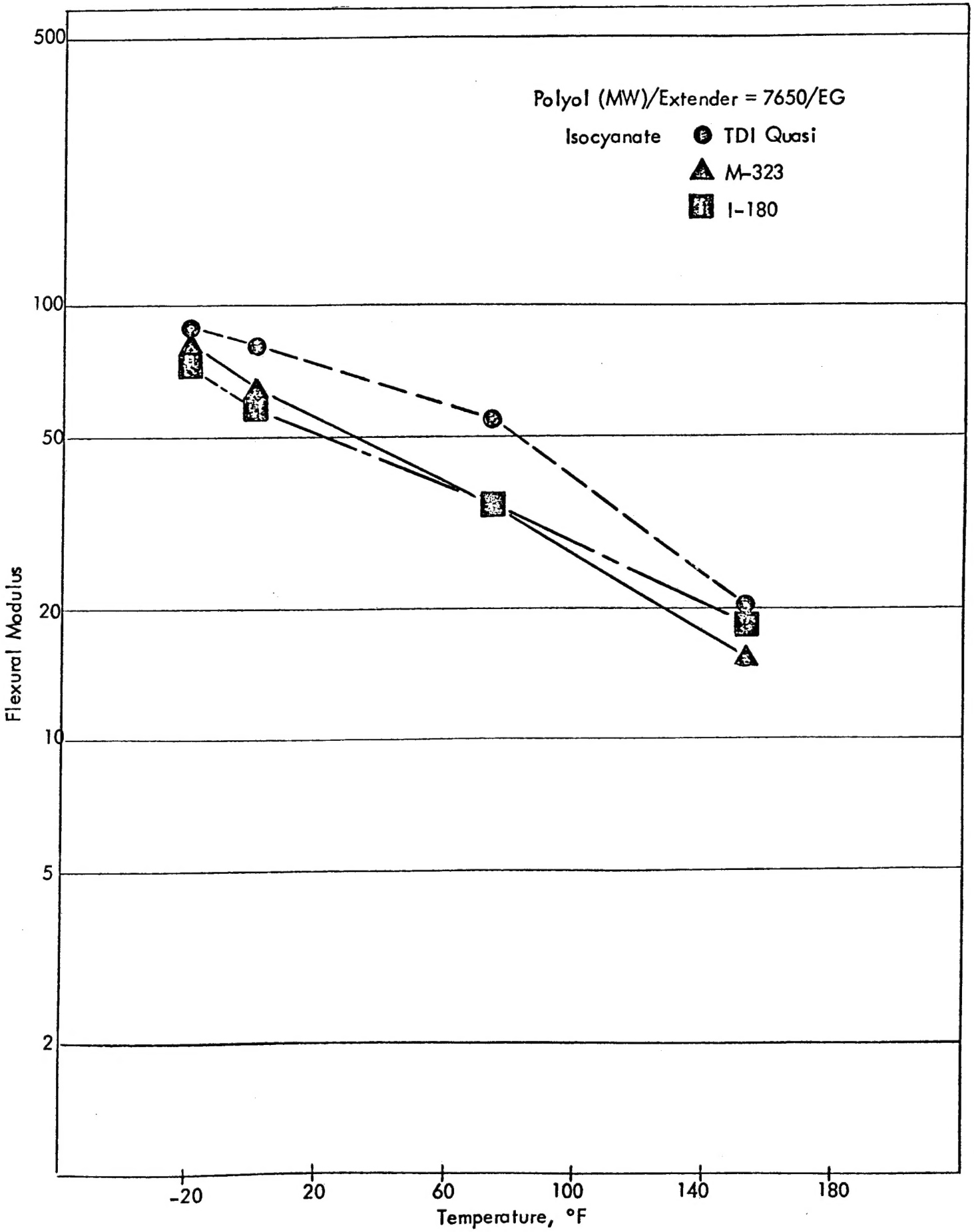


Figure 9

Effect of EG and isocyanate type on the modulus/temperature performance of a urethane elastomer



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